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## PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

CIBA SPECIALTY CHEMICALS WATER  
TREATMENTS LIMITED  
Patents Department  
Cleckheaton Road, Low Moor  
Bradford  
West Yorkshire BD12 0JZ  
ROYAUME-UNI

Date of mailing (day/month/year)

26 July 2002 (26.07.02)

Applicant's or agent's file reference

21923/AC 533

International application No.

PCT/EP01/00391

International filing date (day/month/year)

15 January 2001 (15.01.01)

## - IMPORTANT NOTIFICATION

1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address

RAISTRICK, Lee  
8 Woodward Close  
Allerton  
Bradford  
West Yorkshire BD15 7WJ  
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address

RAISTRICK, Lee  
78 Sefton Avenue  
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Brighouse  
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HD6 2NA  
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned  
☐ the International Searching Authority ☒ the elected Offices concerned  
☐ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Lazar Joseph PANAKAL

Telephone No.: (41-22) 338.83.38

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REC'D 30 JAN 2002

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 21923/A/AC 533	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP01/00391	International filing date (day/month/year) 15/01/2001	Priority date (day/month/year) 28/01/2000
International Patent Classification (IPC) or national classification and IPC C08F2/48		
Applicant CIBA SPECIALTY CHEMICALS WATER TREATMENTS Ltd		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.  
☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.



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3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 08/08/2001	Date of completion of this report
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Simmerl, R Telephone No. +49 89 2399 8515 

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP01/00391

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):  
**Description, pages:**

1-13 as originally filed

**Claims, No.:**

1-19 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP01/00391

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims 1-18
	No: Claims 19
Inventive step (IS)	Yes: Claims 1-18
	No: Claims 19
Industrial applicability (IA)	Yes: Claims 1-19
	No: Claims

2. Citations and explanations  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims; description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/EP01/00391

**Ad section V.:**

1. The subject-matter of claims 1-18 is novel and based on an inventive step (Art. 33(2) and (3) PCT).

Document US-A-5 185 385 (D1) describes a polymerization process which is a combination of a photochemical and a thermal process. In the first step, the monomers are polymerized photochemically. This brings the temperature of the monomer mixture to the temperature required for the chemical initiator to dissociate into free radicals.

D1 neither discloses nor suggest the present process wherein a monomer mixture comprising an ultra violet initiator is polymerized thermally in the absence of ultra violet radiation and wherein the formed polymer is post-treated with ultra-violet radiation. This leads to a reduction of residual monomer which problem is not mentioned in D1.

2. Independent product claim 19 is not novel (Art. 33(2) PCT). It should be noted that product is not rendered novel merely by the fact that it is produced by means of a new process. At present, there is no indication that the present products are different in any respect from those described in D1 or from any other water soluble or water swellable polymer known in the art.
3. Industrial Applicability (Art. 33(4) PCT): o.k.

**Ad section VIII.:**

1. Independent claim 17 contains all features of independent claim 1 but does not contain a corresponding reference (Rule 6.4 PCT).

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>21923/AC 533</b>	<b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. <b>PCT/EP 01/00391</b>	International filing date (day/month/year) <b>15/01/2001</b>	(Earliest) Priority Date (day/month/year) <b>28/01/2000</b>
Applicant  <b>CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

## INTERNATIONAL SEARCH REPORT

Intern: Application No

PCT/EP 01/00391

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F2/48 C08F2/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 185 385 A (R. KANLUEN) 9 February 1993 (1993-02-09)	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

27 April 2001

Date of mailing of the international search report

10/05/2001

Name and mailing address of the ISA

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Cauwenberg, C



### Information on patent family members

PCT/EP 01/00391

Form PCT/ISA/210 (patent family annex) (July 1992)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
2 August 2001 (02.08.2001)

PCT

(10) International Publication Number  
**WO 01/55228 A1**

(51) International Patent Classification<sup>7</sup>: C08F 2/48, 2/10

(21) International Application Number: PCT/EP01/00391

(22) International Filing Date: 15 January 2001 (15.01.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0001883.8 ✓ 28 January 2000 (28.01.2000) GB

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(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMERISATION PROCESS

(57) Abstract: A process of preparing water soluble or water swellable polymer comprising the steps, (a) forming an aqueous mixture comprising, (i) a water soluble ethylenically unsaturated monomer or blend of monomers and, (ii) an ultra violet initiator, (b) effecting polymerisation by subjecting the aqueous mixture formed in step (a) to polymerisation conditions to form a polymer of said monomer or monomer blend, (c) subjecting the polymer formed in step (b) to ultra violet light radiation, characterised in that the polymerisation step (b) is conducted substantially in the absence of ultra violet radiation. In one preferred aspect the ultra violet initiator is distributed throughout the polymer formed in step (b). In another preferred aspect the step (c) is conducted ultra violet light at an intensity of up to 500 milli Watts/cm<sup>2</sup>. Also claimed is a method of reducing the residual monomer content in a water soluble or water swellable polymer by subjecting the polymer to ultra violet irradiation in the presence of an ultra violet initiator. The process is particularly suitable for making highly effective water soluble and water swellable polymers useful as flocculants, coagulants, rheology modifiers, dispersants, superabsorbents and binders etc.

WO 01/55228 A1

### Polymerisation Process

The present invention relates to a process for making water soluble or water swellable polymers, by polymerisation of water soluble ethylenically unsaturated monomer or monomer blend. In particular the invention relates to processes of making said polymers containing low concentrations of residual monomer.

Water soluble and water swellable polymers are used in numerous industrial applications, for instance, flocculants, coagulants, rheology modifiers, dispersants, superabsorbents and binders. Of particular importance are high molecular weight water soluble polymeric flocculants which may be used as retention or drainage aids in paper making or to flocculate sludges such as sewage sludge, waste waters, textile industry effluents red mud from the Bayer Alumina process and suspensions of coal tailings etc.

It is standard practice to prepare water soluble or water swellable polymers by polymerising water soluble monomers using a suitable initiator system. The polymers are usually provided either as a solid particulate product or as a reverse phase dispersion or emulsion. Typically particulate polymers are prepared introducing initiators into an aqueous solution of the monomers and polymerising to form a polymer gel which is then cut into smaller pieces, dried and then ground to the appropriate particle size. Alternatively the polymers are produced as beads by suspension polymerisation or as a water-in-oil emulsion or dispersion by water-in-oil emulsion polymerisation, for example according to a process defined by EP-A-150933, EP-A-102760 or EP-A-126528.

It is known to produce water soluble and water swellable polymers using a variety of initiator systems. For instance it is common practice to polymerise water soluble monomers using redox initiator couples, in which radicals are generated by admixing with the monomer a redox couple which is a reducing agent and an oxidising agent. It is also conventional practice to use either alone or in combination with other initiator systems a thermal initiator, which would include

any suitable initiator compound that releases radicals at an elevated temperature. Other initiator systems include photo and radiation induced initiator systems, which require exposure to radiation to release radicals thereby effecting polymerisation. Other initiator systems are well known and well documented in the literature.

Although water soluble and water swellable polymers can be prepared using many of the commercially available initiator systems, it is often difficult to prepare on an industrial scale polymers which have the correct molecular weight in combination with other desired characteristics, such as solubility, degree of absorbency etc. Over the last ten to fifteen years it has also become increasingly important to provide polymers which have extremely low levels of residual free monomer. This is particularly the case for polymers based on acrylamide monomer.

There have been various proposals in the literature for reducing residual free monomer concentrations in polymers, especially polymers of acrylamide. For instance in US-A-4906732 and US-A-4996251 polyacrylamides are treated with an amidase enzyme which is active towards acrylamide. However, although it was possible to achieve very low levels of free acrylamide, the enzymes proposed in these patents cannot consistently especially at elevated temperatures.

WO-A-97 29136 describes an amidase enzyme which is particularly effective at high temperatures and thus can be applied to the hot polymer gel substantially immediately prior to the drying stage. However, although this enzyme has shown particular advantages over other known amidases, it is still nonetheless difficult to consistently achieve low residual levels of acrylamide on an industrial scale.

Therefore there exists a need to be able to conveniently and consistently provide water soluble or swellable polymers with no or extremely low levels of residual monomer, especially acrylamide monomer.

There also exists a need to achieve this in an industrial scale process and in particular in a process which does not require additional long residence stages in the production process.

According to one aspect of the invention we provide a process of preparing water soluble or water swellable polymer comprising the steps,

(a) forming an aqueous mixture comprising,

(i) a water soluble ethylenically unsaturated monomer or blend of monomers and,

(ii) an ultra violet initiator,

(b) effecting polymerisation by subjecting the aqueous mixture formed in step (a) to polymerisation conditions to form a polymer of said monomer or monomer blend, wherein ultra violet initiator is distributed throughout the polymer,

(c) subjecting the polymer formed in step (b) to ultra violet light radiation, characterised in that the polymerisation step (b) is conducted substantially in the absence of ultra violet radiation.

Although higher levels of ultra violet radiation may be employed generally step (c) is conducted using fairly low levels of ultra violet radiation intensity, for instance up to  $1 \text{ Watt/cm}^2$ , usually below  $500 \text{ milli Watts/cm}^2$ .

According to a further aspect of the invention we provide a process of preparing water soluble or water swellable polymer comprising the steps,

(a) forming an aqueous mixture comprising,

(i) a water soluble ethylenically unsaturated monomer or blend of monomers and,

(ii) an ultra violet initiator,

(b) effecting polymerisation by subjecting the aqueous mixture formed in step (a) to polymerisation conditions to form a polymer of said monomer or monomer blend,

(c) subjecting the polymer formed in step (b) to ultra violet light radiation at an intensity of up to 500 milli Watts, characterised in that the polymerisation step (b) is conducted substantially in the absence of ultra violet radiation.

The advantage of being able to use relatively low levels of radiation intensity is that there is a reduced risk of inducing denaturing of the polymer. One effect of denaturing the polymer may be undesirable or uncontrolled cross-linking or unacceptable loss of solubility. This may be particularly important when preparing high molecular weight water soluble polymers, where cross-linking and/or loss of solubility could have a deleterious effect on performance. To a certain extent exposure to high levels of ultra violet radiation may be detrimental to deliberately cross-linked polymers in that the additional cross-linking would be uncontrolled and could also lead to a loss of performance. Thus for a cross-linked superabsorbent polymer excessive exposure to ultra-violet cross-linking may result in excessive cross-linking which could impair the absorbency characteristics.

Thus it is preferred that very low levels of UV radiation intensity are used, for instance up to 100 milli Watts/cm<sup>2</sup>. Generally the levels of intensity will be above 5 or 10 milli Watts/cm<sup>2</sup>. Intensities of below 50 milli Watts/cm<sup>2</sup> are generally preferred, for instance in the range of 30 to 40 milliWatts/cm<sup>2</sup>.

The water soluble or water swellable polymer is prepared by polymerisation of a water soluble monomer or water soluble monomer blend. By water soluble we mean that the water soluble monomer or water soluble monomer blend has a solubility in water of at least 5g in 100 ml of water, measured at 25°C. The polymerisation step (b) may employ conventional polymerisation techniques, provided that these do not result in exposure to ultra violet light.

The polymerisation step (b) may be effected by subjecting the aqueous monomer solution to any conventional polymerisation conditions which do not involve exposure to ultra violet radiation. Desirably this may be achieved by the use of

redox initiators and/or thermal initiators. Typically redox initiators include a reducing agent such as sodium sulphite, sulphur dioxide and an oxidising compound such as ammonium persulphate or a suitable peroxy compound, such as tertiary butyl hydroperoxide etc. Redox initiation may employ up to 10,000 ppm (based on weight of monomer) of each component of the redox couple. Preferably though each component of the redox couple is often less than 1000 ppm, typically in the range 1 to 100 ppm, normally in the range 4 to 50 ppm. The ratio of reducing agent to oxidizing agent may be from 10:1 to 1:10, preferably in the range 5:1 to 1:5, more preferably 2:1 to 1:2, for instance around 1:1.

Polymerisation step (b) may also be effected by employing a thermal initiation alone or in combination with other initiator systems, for instance redox initiators. Thermal initiators would include any suitable initiator compound that releases radicals at an elevated temperature, for instance azo compounds, such as azobisisobutyronitrile (AZDN), 4,4'-azobis-(4-cyanovaleric acid) (ACVA). Typically thermal initiators are used in an amount of up to 10,000 ppm, based on weight of monomer. In most cases, however, thermal initiators are used in the range 100 to 5,000 ppm preferably 200 to 2,000 ppm, usually around 1,000 ppm.

The water soluble or water swellable polymer prepared according to the process of the present invention may be cationic, anionic, nonionic or amphoteric. It may be substantially linear or alternatively branched or cross-linked. Cross-linked or branched polymers are prepared by incorporating a branching or cross-linking agent into the monomer blend. The cross-linking or branching agent may be for instance a di- or multifunctional material that reacts with functional groups pendant on the polymer chain, for instance multivalent metal ions or amine compounds which can react with pendant carboxylic groups. Preferably, however, the cross-linking or branching agent will be a polyethylenically unsaturated compound, which becomes polymerised into two or more polymer chains. Typically such cross-linking agents include methylene-bis-acrylamide, tetra allyl ammonium chloride, tri-allyl amine and polyethylene glycol di acrylate. The polymers may be highly crosslinked and therefore water insoluble but water swellable. Alternatively the

polymer may be water soluble and either substantially linear or slightly branched, for instance prepared using less than 10 ppm cross-linking/branching monomer.

The water soluble or water swellable polymer may be cationic, anionic, amphoteric or non-ionic. Anionic polymers may be formed from one or more ethylenically unsaturated anionic monomers or a blend of one or more anionic monomers with for instance a nonionic monomer, preferably acrylamide. The anionic monomers include acrylic acid, methacrylic acid, maleic acid, crotonic acid, itaconic acid, vinylsulphonic acid, allyl sulphonic acid, 2-acrylamido-2-methylpropane sulphonic acid and salts thereof. A preferred anionic polymer is the copolymer of sodium acrylate with acrylamide.

Cationic polymers may be formed from one or more ethylenically unsaturated cationic monomers optionally with for instance a nonionic monomer, preferably acrylamide. The cationic monomers include dialkylamino alkyl (meth) acrylates, dialkylamino alkyl (meth) acrylamides, including acid addition and quaternary ammonium salts thereof, diallyl dimethyl ammonium chloride. Preferred cationic monomers include the methyl chloride quaternary ammonium salts of dimethylamino ethyl acrylate and dimethyl aminoethyl methacrylate.

Amphoteric polymers include at least one cationic monomer (for example as defined above) and at least one anionic monomer (for example as defined above) optionally with a nonionic monomer, especially acrylamide.

Non-ionic polymers include polymers of any suitable non-ionic monomers, for instance, acrylamide, methacrylamide, N-vinylpyrrolidone and 2-hydroxyethyl acrylate. Preferred non-ionic polymers comprise acrylamide especially acrylamide homopolymers.

Preferably, the water soluble or water swellable polymers comprise acrylamide.



The polymer produced by the process of the present invention may be a relatively low molecular weight polymer, for instance polymerised to a molecular weight below 100,000, for instance 2,000 to 10,000. Preferably however, the polymers are relatively higher molecular weight, for instance at least 100,000, especially at least 500,000. Typically the polymer has a molecular weight in the range of above 1 million to 20 or 30 million or higher. In general these high molecular weight polymers tend to exhibit high intrinsic viscosities (IV), for instance at least 3 dl/g (measured at various polymer concentrations using standard techniques in 1N NaCl buffered to pH 7.5 at 25°C). Preferably the polymer has an IV of at least 4 dl/g often at least 7 or 8 dl/g, for instance at least 12 dl/g. In some cases it may be highly desirable for the polymer to have an IV as high as 20 or 30 dl/g or even higher. However especially preferred polymers have an IV in the range 8 to 18 dl/g.

Typically an aqueous solution of water soluble monomer may be polymerised by solution polymerisation to provide an aqueous gel or by reverse phase polymerisation in which an aqueous solution of monomer is suspended in a water immiscible liquid and polymerised to form polymeric beads or alternatively by emulsifying aqueous monomer into an organic liquid and then effecting emulsion polymerisation. Examples of reverse phase polymerisation are given in EP-A-150933, EP-A-102760 or EP-A-126528. Preferably the polymer is prepared by solution polymerisation.

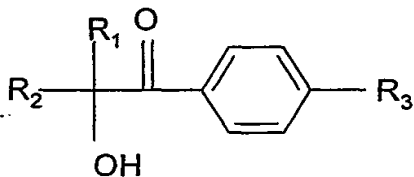
The process of the present invention requires that an aqueous monomer mixture is first formed comprising (i) a water soluble ethylenically unsaturated monomer or blend of monomers and (ii) an ultra violet initiator. In addition the aqueous monomer mixture may also contain other components, for instance redox initiators or thermal initiators or other compounds that may assist with the polymerisation step (b). The aqueous monomer mixture may also comprise other ingredients, for instance chain transfer agents which may be required to regulate the chain length.

The ultra violet initiator (ii) comprised in the aqueous monomer mixture may be any suitable initiator that remains substantially inert during the polymerisation step (b). Therefore the ultra violet initiator would generally be unsuitable if it decomposed during this initial polymerisation step. Therefore it is desirable to choose an ultra violet initiator that is not temperature sensitive at a temperature reached during the initial polymerisation step.

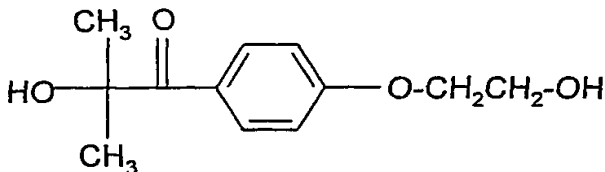
Desirably the ultra violet initiator is distributed homogenously throughout the aqueous monomer mixture, in order that it is evenly distributed throughout the resulting polymer. Preferably the ultra violet initiator is soluble or dispersible in the aqueous monomer or monomer blend.

We have surprisingly found that effective polymers can be produced by the process of the present invention, wherein an aqueous monomer blend which also contains an ultra violet initiator is first subjected to polymerisation in the absence of ultra violet light in which the ultra violet initiator remains substantially inert and then subjecting the polymer to ultra violet radiation.

Preferably the ultra violet initiator is a compound of formula:

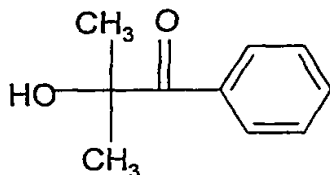


wherein  $\text{R}_1$  and  $\text{R}_2$  are each independently  $\text{C}_{1-3}$  alkyl or together form a  $\text{C}_{4-8}$  cycloaliphatic ring,  $\text{R}_3$  is H,  $\text{C}_{1-2}$  alkyl or  $-\text{O}(\text{CH}_2\text{CH}_2)_n\text{OH}$  and  $n$  is 1-20. An especially preferred ultra violet initiator is the compound defined by the formula,



known as 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one supplied as Irgacure ® 2959 photoinitiator by Ciba Specialty Chemicals.

Another especially preferred UV initiator is the compound of the formula,



known as 1-phenyl-2-hydroxy-2-methyl-1-propane-1-one supplied as Darocure ® 1173 photoinitiator by Ciba Specialty Chemicals.

Desirably the ultra violet initiator is used in an amount up to 10,000 ppm by weight of monomer. However, for economic reasons it is usually preferred not to use more than about 5,000. Suitable results are often obtained when the ultra violet initiator is included in an amount in the range 50 to 3,000 ppm, more preferably 100 to 2,500 ppm, especially 500 to 2,000 ppm.

The process involves the step of subjecting the polymer formed in the polymerisation step (b) to ultra violet radiation. This may be done by passing the formed polymer under ultra violet lamps. For instance the polymer may be passed from the reactor vessel and then irradiated with a suitable dose of ultra violet light and then passed to a drying section. Alternatively the polymer may be exposed to ultra violet radiation in the reactor vessel. Preferably the polymer is subjected to the ultraviolet light in the drying section. Thus in this preferred form of the invention ultra violet lamps are mounted such that the polymer is exposed to ultra violet light whilst inside the drying equipment. More preferably the drying equipment is a fluid bed dryer and the ultra violet lamps are mounted inside the dryer.

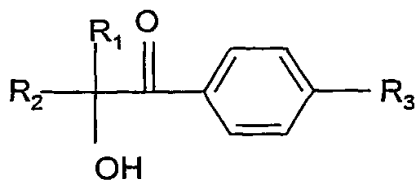
It has further surprisingly been found that a water soluble or water swellable polymer in which the amount of residual monomer is below 100 ppm is obtainable

by the process of the present invention, including any of the more specific embodiments.

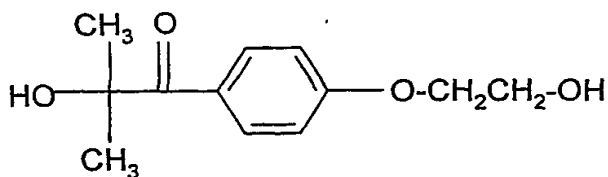
According to a further aspect of the invention we provide a method of reducing the residual monomer content in a water soluble or water swellable polymer by subjecting the polymer to ultra violet irradiation in the presence of an ultra violet initiator. The ultra violet initiator may be applied to the surface of the formed polymer and allowed to coat the surface of the polymer particles and then subjecting the polymer to ultra violet radiation. In a preferred form of this aspect of the invention the ultra violet initiator is actually absorbed into the polymer and is then preferably distributed throughout the polymer before being subjected to irradiation by ultra violet light. Alternatively the water soluble or water swellable polymer may be formed containing the ultra violet initiator distributed throughout the polymer. This may be for instance as a result of carrying out a process in accordance with the first aspect of the invention.

Preferably the method of reducing residual monomer is applied to polymers of acrylamide and said acrylamide polymer contains residual acrylamide monomer. More preferably the polymer of acrylamide is a relatively high molecular weight polymer and has an intrinsic viscosity of at least 4 dl/g, often at least 7 or 8 dl/g, for instance at least 12 dl/g. In some cases it may be highly desirable for the polymer of acrylamide to have an IV as high as 20 or 30 dl/g or even higher. Especially preferred are polymers of acrylamides which have an IV in the range 8 to 18 dl/g.

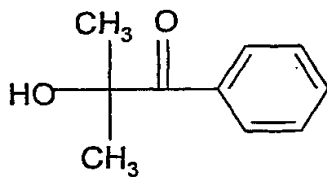
The ultra violet initiator may be any suitable ultra violet initiator as given herein before. It is preferred that the ultra violet initiator is water soluble or at least water dispersible. Preferably the ultra violet initiator is a compound of formula,



wherein  $R_1$  and  $R_2$  are each independently  $C_{1-3}$  alkyl or together form a  $C_{4-8}$  cycloaliphatic ring,  $R_3$  is H,  $C_{1-2}$  alkyl or  $-O(CH_2CH_2)_nOH$  and  $n$  is 1-20. Most preferably the ultra violet initiator either a compound of formula,



or a compound of formula



The following examples illustrate the invention, but are not intended to in any way limit the scope of the invention.

### Examples

#### Test 1

Two tonnes of aqueous monomer mixture is prepared comprising 90% by weight acrylamide and 10% by weight dimethylaminoethyl acrylate methyl chloride quaternary ammonium salt and having a total monomer concentration of about 30%. Nitrogen gas is passed through the aqueous medium in order to remove dissolved oxygen or other volatile reactive species. 4.5 ppm potassium bromate  $\text{KBrO}_3$  and 9ppm sodium sulphite  $\text{Na}_2\text{SO}_3$  is combined with the aqueous monomer and mixed thoroughly. Polymerisation is allowed to proceed for two hours and the resulting polymer is dried using a fluid bed dryer.

#### Test 2

This is repeated but subjecting the gel to ultra violet radiation for 20 minutes during the drying process using a UV flood system from Starna using an intensity of  $2 \times 10^{-4} \mu\text{W}/\text{cm}^2/\text{nm}$ . The equivalent irradiation will be obtained using a Solartell Solarscope, model 1 with a multidirectional probe, using an intensity of 25milli Watts/ $\text{cm}^2$ . These tests are repeated using various amounts of 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure ® 2959) in the monomer mixture.

#### Tests 3 to 6

The solubility, solution viscosity and residual acrylamide monomer are assessed and the results are shown in Table 1.

Table 1

Test	UV initiator (ppm)	UV irradiation (min)	1% solution viscosity (cP)*	Solubility	Residual Acrylamide (ppm)
1	0	0	188	Good	881
2	0	20	199	Good	452
3	500	0	194	Good	964
4	500	20	182	Fair/Good	57
5	2000	0	176	Fair/good	960
6	2000	20	166	Good	47

measured using a Mettler viscometer at a shear rate of  $30^{-s}$ , measured at 25°C.

Examples 7 to 12

Examples 1 to 6 are repeated but using a an aqueous solution of acrylamide monomer. Viscosity and residual acrylamide concentrations are shown in Table 2.

Table 2

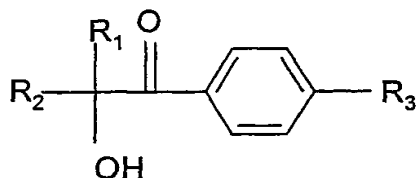
Test	UV initiator (ppm)	UV irradiation (min)	1% solution viscosity (cP)#	Residual Acrylamide (ppm)
1	0	0	28	532
2	0	20	24	412
3	500	0	26	552
4	500	20	24	38
5	2000	0	28	639
6	2000	20	24	32

# measured using a Mettler viscometer at a shear rate of  $250^{-s}$ , measured at 25°C.

Claims

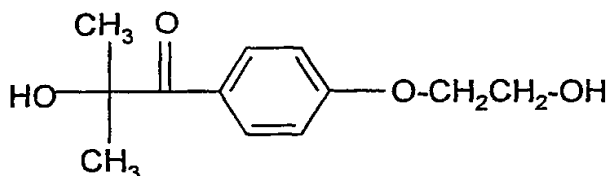
1. A process of preparing water soluble or water swellable polymer comprising the steps,
  - (a) forming an aqueous mixture comprising,
    - (i) a water soluble ethylenically unsaturated monomer or blend of monomers and,
    - (ii) an ultra violet initiator,
  - (b) effecting polymerisation by subjecting the aqueous mixture formed in step (a) to polymerisation conditions to form a polymer of said monomer or monomer blend, wherein ultra violet initiator is distributed throughout the polymer,
  - (c) subjecting the polymer formed in step (b) to ultra violet light radiation, characterised in that the polymerisation step (b) is conducted substantially in the absence of ultra violet radiation.
2. A process according to claim 1 in which the polymerisation step (b) is effected by suitable polymerisation initiators, selected from the group consisting of redox initiators and thermal initiators.
3. A process according to claim 1 or claim 2 in which the polymer in step (c) is subjected to ultraviolet light radiation at an intensity of up to 500 milliWatts.
4. A process according to any of claims 1 to 3 in which the polymer is formed from acrylamide.
5. A process according to any of claims 1 to 4 in which the polymer has an intrinsic viscosity of at least 4 dl/g.
6. A process according to any of claims 1 to 5 in which the polymer formed by solution polymerisation.
7. A process according to any of claims 1 to 6 in which the ultra violet initiator is soluble or dispersible in the aqueous monomer or monomer blend.
8. A process according to any of claims 1 to 7 in which the ultra violet initiator is a compound of formula:



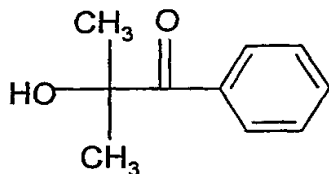


wherein  $R_1$  and  $R_2$  are each independently  $C_{1-3}$  alkyl or together form a  $C_{4-8}$  cycloaliphatic ring,  $R_3$  is H,  $C_{1-2}$  alkyl or  $-O(CH_2CH_2)_nOH$  and  $n$  is 1-20.

9. A process according to claim 8 in which the ultra violet initiator is a compound of formula:



10. A process according to claim 8 in which the ultra violet initiator is a compound of formula:

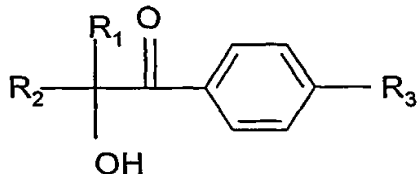


11. A process according to any of claims 1 to 10 in which step (c) is conducted simultaneous with a drying stage.

12. A method of reducing the residual monomer content in a water soluble or water swellable polymer by subjecting the polymer to ultra violet irradiation in the presence of an ultra violet initiator.

13. A method according to claim 12 in which the polymer is a polymer of acrylamide of intrinsic viscosity above 4 dl/g.

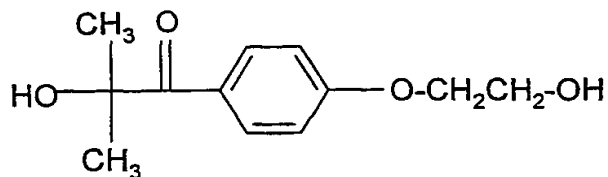
14. A method according to claim 12 or claim 13 in which the ultra violet initiator is a compound of formula:



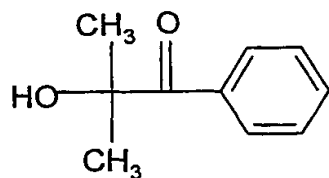
wherein  $R_1$  and  $R_2$  are each independently  $C_{1-3}$  alkyl or together form a  $C_{4-8}$

cycloaliphatic ring,  $R_3$  is H,  $C_{1-2}$  alkyl or  $-O(CH_2CH_2)_nOH$  and  $n$  is 1-20.

15. A method according to claim 14 in which the ultra violet initiator is a compound of formula:



16. A method according to claim 15 in which the ultra violet initiator is a compound of formula:



17. A process of preparing water soluble or water swellable polymer comprising the steps,

(a) forming an aqueous mixture comprising,

(i) a water soluble ethylenically unsaturated monomer or blend of monomers and,

(ii) an ultra violet initiator,

(b) effecting polymerisation by subjecting the aqueous mixture formed in step (a) to polymerisation conditions to form a polymer of said monomer or monomer blend,

(c) subjecting the polymer formed in step (b) to ultra violet light radiation at an intensity of up to 500 milli Watts, characterised in that the polymerisation step (b) is conducted substantially in the absence of ultra violet radiation.

18. A process according to claim 17 in which the ultra violet light radiation is at an intensity of up to 50 milli Watts.

19. A water soluble or water swellable polymer obtainable by a process defined by any of claims 1 to 11, 17 or 18 or by a method according to anyone of claims 12 to 16 in which the amount of residual monomer is below 100 ppm.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/25528

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F6/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 41 23 889 A (SANYO CHEMICAL IND LTD) 12 March 1992 (1992-03-12) abstract; claims; examples 8,10; table 1 page 5, line 48 - line 54	1-30
Y	DATABASE WPI Section Ch, Week 198236 Derwent Publications Ltd., London, GB; Class A14, AN 1982-75091E XP002156085 & JP 57 121009 A (SUMITOMO CHEM CO LTD), 28 July 1982 (1982-07-28) cited in the application abstract	1-30

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

20 December 2000

Date of mailing of the international search report

05/01/2001

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/25528

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 197 48 153 A (STOCKHAUSEN CHEM FAB GMBH) 6 May 1999 (1999-05-06) cited in the application abstract; claims -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/25528

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		BR 9813338 A	22-08-2000
		WO 9923120 A	14-05-1999
		EP 1025133 A	09-08-2000
		NO 20002294 A	28-04-2000